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NOTICE OF ENTITLEMENT

BYRON AGRICULTURAL COMPANY PTY LTD, the applicant and nominated person in respect of Application No. 42800/89 state the following:-

The Nominated Person is entitled to the grant of the patent because the Nominated Person derives title to the invention from the inventors VICTOR MARCUS LEWIS and DAVID ADRIAN LEWIS by assignment.

DATED this 17th day of January, 1992.

Hecker Cummings

.....
a member of the firm of
DAVIES COLLISON CAVE for
and on behalf of the
applicant(s).

PATENT APPLICATION FORM
COMMONWEALTH OF AUSTRALIA

Patents Act 1952

Regulation 9

622225

We, BYRON AGRICULTURAL COMPANY PTY. LTD.

of 19A Boundary Street, Ruchcutters Bay, NSW, 2011

hereby apply for the grant of a Standard Patent for an invention
entitled LOW-TEMPERATURE STABLE VEGETABLE PRODUCTS

which is described in the accompanying provisional specification.

Our address for service is ARTHUR S. CAVE & CO., Patent and Trade
Mark Attorneys, Level 10, 10 Barrack Street, Sydney, New South
Wales, Australia 2000.

Dated this 13th day of October, 1988.

BYRON AGRICULTURAL
COMPANY PTY. LTD.
By Its Patent Attorneys,
ARTHUR S. CAVE & CO.



P.R. TAYLOR F.I.P.A.A.

To:
Commissioner of Patents

ARTHUR S. CAVE & CO.
PATENT AND TRADE MARK ATTORNEYS
SYDNEY

ASC 1

(54) Title
VEGETABLE PRODUCTS WITH IMPROVED STABILITY AT FREEZER TEMPERATURES AND
PROCESS FOR PRODUCING SAME

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(56) Prior Art Documents
US 3219461
US 4478868

(57) Claim

1. A method for preserving a vegetable product at sub-zero temperatures which comprises firstly treating said product by partially dehydrating and adding to said product at least one water activity controlling substance whereby the water activity is less than 1 (measured at 20°C), the moisture content is less than that of the untreated vegetable product, and both said water activity and moisture content is within a range whereby said product remains flexible and unfrozen at typical sub-zero frozen food storage temperatures, and secondly reducing the temperature of said product to a typical sub-zero frozen food storage temperature.

8. Vegetable product preserved at a typical sub-zero frozen food storage temperature which has been partially dehydrated and to which at least one water activity controlling substance has previously been added, characterized in that said product has a water activity less than 1 (measured at 20°), a moistur

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-2-

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content less than that of the unpreserved vegetable product,
and both said water activity and moisture content is within a
range whereby said product remains flexible and unfrozen at
typical sub-zero frozen food storage temperatures.

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COMPLETE SPECIFICATION

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TO BE COMPLETED BY APPLICANT

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AUSTRALIA

Complete Specification for the invention entitled VEGETABLE
PRODUCTS WITH IMPROVED STABILITY AT FREEZER TEMPERATURES AND
PROCESS FOR PRODUCING SAME.

The following statement is a full description of this invention
including the best method of performing it known to me:-

- 1 -

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VEGETABLE PRODUCTS WITH IMPROVED STABILITY AT
FREEZER TEMPERATURES AND PROCESS FOR PRODUCING SAME

The present invention relates to a new type of low temperature stable vegetable product and a process for the production thereof.

Many processes are known for the preserving and storage of foods for short-term and long-term periods of time. Freezing is one such process.

Frozen food products, in particular vegetables and vegetable products, are important products of commerce having use in industrial, consumer, and food service markets. While the quality and acceptability of frozen vegetables is generally regarded as satisfactory, several inherent disadvantages are encountered with this type of food storage.

After having been frozen, food products, including vegetables, must be kept at sub-zero (Celsius) temperatures. Frozen food products which have been allowed to thaw partially or fully and are then refrozen suffer severe loss of quality. Frozen food products that have been allowed to thaw either accidentally or if thawed for a period awaiting use can present a spoilage and public health hazard.

While some products such as peas, beans and carrot dice can be individually quick frozen, other vegetables will freeze into a solid block which needs to be thawed so that measured quantities can be used. Even individually quick frozen vegetables tend to agglomerate into lumps on storage as a result of water freezing between the vegetable pieces.

The energy required to freeze the water in vegetables is

considerable and as well as this cost, freezer storage is expensive, as is freezer transport. Freezer transport is always precarious so far as maintaining the product in a frozen condition is concerned.

Some of the costs involved in storage and transport can be reduced considerably by the known process of "d hydrofreezing". In this process, vegetables are dehydrated to as much as 30% of their original weight, and are then frozen. Dehydrofreezing can reduce freezing, packing, storage and transport costs by up to 60%. However, the products still freeze hard, with consequent loss of texture and, having higher solids contents than normal, the products thaw more readily. This can lead to problems of spoilage of the thawed product in much the same way as for thawed conventionally frozen products.

Various methods of vegetable dehydration are known and several are used industrially. In most of these methods the vegetables are dried to low moisture contents, usually below 7%, and in the case of freeze-dried vegetables the vegetables are dried often as low as 2% to 3%. At these moisture contents the vegetables are hard and very brittle. There is a great deal of breakage and excessive production of fines (small vegetables pieces and fibres). This is particularly so with leafy vegetables. Normal air-dried vegetables which are exposed to relatively high storage temperatures at low moisture contents for long periods of time suffer substantial flavour, colour and aroma deterioration.

Stable dehydrated veg tables having higher than normal moisture contents can be produced by the addition of salt to

lower the water activity of partially dried vegetables, as described by Lewis and Lewis (Australian Patent No. 532414, US Patents 4,447,460 and 4,683,141). With these the upper moisture level is 25%, but in general longer shelf stability is attained at moisture levels at the lower end of the moisture scale.

Onions for instance, tend to discolour slowly when stored at moisture levels above 10%. At moisture contents of 10% or lower the onion slices are brittle enough to allow breakage of the slices. Many dehydrated white vegetables or the pale tissues of other vegetables, for example the inner petioles of celery, the white tissue of zucchini, the inner pale yellow leaves of cabbage or Chinese cabbage and white cucumber tissue will darken relatively quickly in storage. Furthermore, many green and pale-green vegetables, whether in solute-added or conventionally dried form, suffer deterioration of the green chlorophyll pigment when stored at ambient temperatures at water activities above 0.50 for more than a few months. Still other vegetables, particularly the leafy ones, become brittle and fragile when dehydrated in any form and, as a result, are only available as flakes or powders. Examples of such products includes spinach, parsley, sweet basil, cabbage, leeks, and similar types of vegetables and herbs.

The shelf-life of dehydrated vegetable products can be increased by storage at low temperatures. At lower storage temperatures the rates of the chemical reactions leading to deterioration are reduced. However, at freezer storage temperatures, generally between 0°C and -25°C, the normal

dehydrated and solute added products become even more brittle and subject to breakage.

A number of food products that can be stored at freezer temperatures without freezing have been described. These include batters (Kahn et al U.S. Patent 4,154,863) emulsion cream type products (Kahn et al U.S. 4,313,967) egg yolk (Kahn et al U.S. Patent 4,244,976), fruit juices (Kahn et al U.S. Patent 4,418,082) fruits (Kahn et al U.S. Patent 4,350,711) oil in water emulsions (U.S. Patent 4,387,109) and "whippable" foods (Kahn et al U.S. Patent 4,146,652). These all depend for their non-freeze performance on very high levels of sugars. These levels of sugars would not be compatible with fresh vegetable products.

The addition of solutes to control water activity in intermediate moisture foods is well documented (Lewis et al U.S. Patent 4,447,460, U.S. Patent 4,683,141 and U.S. Patent 4,384,009). Solutes have also been added to foodstuffs to produce frozen foods with particular claimed advantages, Lamb U.S. Patent 3,219,461, Ariss et al U.S. 4,478,868, but not with the aim of producing non-freezable food products.

We have now surprisingly found that very stable, high quality vegetable products, intended for storage at below 0°C, can be produced in a "non-breakable", and flexible form.

The present invention concerns a method for preserving a vegetable product at sub-zero temperatures which comprises firstly treating the product by partially dehydrating and adding to the product at least one water activity controlling substance whereby the water activity is less than 1 (measured

at 20°C), the moisture content is less than that of the untreated vegetable product, and both the water activity and moisture content is within a range whereby the product remains flexible and unfrozen at typical sub-zero frozen food storage temperatures, and secondly reducing the temperature of the product to a typical sub-zero frozen food storage temperature.

The invention also concerns a vegetable product preserved at a typical sub-zero frozen food storage temperature which has previously been partially dehydrated and to which at least one water activity controlling substance has previously been added, characterized in that the product has a water activity less than 1 (measured at 20°), a moisture content less than that of the unpreserved vegetable product, and both the water activity and moisture content is within a range whereby the product remains flexible and unfrozen at typical sub-zero frozen food storage temperatures.

The term "freeze" as used herein is meant to convey a state where ice crystals and/or solute crystals are formed in the product and thus make it hard and/or brittle. The aim of the present invention is to produce products that do not "freeze" in this manner at typical freezer temperatures.

In one preferred form the water activity of the invention is below about 0.90, and more preferably below about 0.85. The water activity may also be above about 0.5 and more preferably above about 0.7. The water activity is measured at 20°C. The actual values for the limits of the water activity will depend on the type of vegetable chosen, as well as factors such as the type and amount of water activity controlling substance added,

and the moisture content of the chosen vegetable.

The moisture content is chosen such that the product remains flexible at typical frozen storage temperatures. The moisture content will preferably be between about 20 and 50%. More preferably the moisture content is between about 25 and 45%.

The final form of the vegetable product produced in accordance with the invention includes sliced vegetables, uncut or coarsley cut leaf vegetables, and other forms of prepared vegetables. These vegetable products are stable at low temperatures, can be stored for short periods of time at temperatures above those typically used for the storage of conventional frozen vegetables, do not readily spoil and do not freeze solid. Also, they will not freeze or become brittle at normal freezer temperatures. In general, suitable typical frozen food storage temperatures will be about -20°C .

The water activity and moisture content is affected by adjusting the composition of vegetables by a combination of dehydration, and the addition of one or more water activity controlling substances, including but not limited to sodium chloride and other salts, sugars such as sucrose, dextrose and invert sugars and polyhydric alcohols such as glycerol.

Prior to the introduction of solutes the vegetables to be treated can be peeled, and blanched or otherwise prepared in accordance with any customary manner and then may be dried in air or vacuum, for example. Solutes may be added by any method including but not limited to presteeping before or after drying, tumbling with known quantities of solute before drying,

or with solutions or solid solutes initially or at intermediate stages.

Solutes may also be added to vegetables by the process described in Australian Patent 532414, for example, by (a) partially dehydrating the vegetables(s) in air or vacuum, (b) introducing, at a suitable stage, one or more water activity controlling solutes into the vegetable(s), and (c) dehydrating the treated vegetable(s) to the desired moisture content.

Alternatively, the water activity controlling substances can be added before, or at the same time as the vegetable pieces are dehydrated. For example, salt may be added and briefly mixed with the vegetable pieces to coat the pieces, which are then partially dehydrated in air or vacuum.

Suitable water activity controlling solutes include sodium chloride, sodium citrate, potassium chloride and other such salts, sugars such as sucrose dextrose and invert sugars, and polyhydric alcohols such as glycerol, sorbitol or propylene glycol, but are not limited to these. If a sugar or sugars are selected as the water activity controlling substance then the total added sugar level is preferably below 15% by weight in the finished product, so that the vegetable product has an acceptable taste.

The concentration of the solutes is dependent on such variables as flavour considerations, the nature of the solutes, and the types of vegetable being treated.

The term "vegetable" as used herein denotes plants and plant parts normally considered as vegetables, and includes leaves, petioles roots, bulbs, corms, tubers, etc. as well as

fruits such as tomatoes, squash, pumpkin and seeds such as sweetcorn or peas etc. The definition of vegetables also includes mixtures of different vegetables.

Water activity depends on the amount of moisture present as well as the amounts of the other substances present in the food. The expression " a_w " is used to describe water activity, and is calculated by the formula:

$$a_w = p/p_o$$

where p is the vapour pressure of the food, and p_o is the vapour pressure of water, at the same temperature.

The final composition of the vegetable product is adjusted by selecting the type and concentration of solute(s) added into the vegetable and adjusting the moisture content of the vegetable product such that when the vegetable product is subjected to sub-zero temperatures as low as -20°C or thereabouts the product will not freeze. The moisture content of the treated vegetable which ensures that it does not freeze will vary with the concentration of solutes added and the nature of these solutes, and may be in the order of 20 to 50%.

In general, the higher the concentration of solutes the lower will be the moisture content at which the vegetable product freezes. If the moisture level is too low, relative to the solutes added, the vegetable product will become hard, brittle and fragile at freezing temperatures due to the crystallization of the solutes. If the moisture content is too high, relative to the solutes, the vegetable pieces will freeze hard due to the formation of ice crystals, the cell structure of the vegetable will be damaged, and the pieces can become

fragile and may matt into a block.

Vegetable products produced in accordance with the present invention are flexible at the time the dehydration process is completed and stay flexible when held at conventional freezer temperatures at which they are to be stored. Furthermore, by judicious selection of the solute(s) and final moisture content, the water activity of these products at +20°C may preferably be adjusted below the level of 0.90 and preferably below 0.85 and may also be above 0.5, preferably 0.7. At such water activity levels, if the vegetable product increases in temperature above zero the vegetable product is not subject to bacterial deterioration, nor is it subject to mycological deterioration at other than a very slow rate. Storage at low temperatures greatly retards changes in colour and flavour and significantly prolongs shelf-life.

Non-freezable dehydrated vegetable products in accordance with the invention have a substantially higher moisture content than conventional dehydrated vegetables and a generally higher moisture content than the solute-added vegetables described in Australian Patent No. 532414. They are therefore subject to shorter processing times, suffer less heat damage and require less energy to dehydrate.

While these non-freezable vegetable products may contain relatively high levels of added water activity controlling substances, they are prepared for use by rehydration and cooking with substantial volumes of water, usually in the ratio of about 10:1. This gives salt and sugar levels in the

products as consumed within the normal seasoning levels. Furthermore, these products rehydrate more rapidly because they are at a higher moisture content than conventional dehydrated vegetables and because the presence of solutes induces the more rapid absorption of water into the vegetable tissue.

The invention is illustrated below by means of the following non-limiting examples.

EXAMPLE 1

Leaves of spinach with a total solids content of 7% were washed to remove grit and dirt and were coarsely cut into strips about 5cm wide. They were dehydrated to approximately 40% moisture. Aliquots of the spinach were then mixed with a solution of salt and sugar in a tumbler for three minutes, the quantity of solutes being calculated to give final contents 5% salt and 10% sugar at moisture contents of 60%, 55%, 45%, 30%, 20% and 15%.

The finished products had the following composition:

<u>Sample</u>	<u>Water Activity</u>	<u>Moisture %</u>	<u>Freeze or Not at -20°C</u>
1	.91	60	Yes
2	.89	55	Yes
3	.86	43	No
4	.75	28	No
5	.58	17	No
6	.40	14	Yes

Samples 3, 4 and 5 had a soft texture and rehydrated instantly when covered with boiling water to give spinach of excellent flavour, colour and texture. The pieces of leaf were in the same whole large piece as they were before dehydration.

EXAMPLE 2

Parsley leaves of the "curley" variety were removed from the coarse stems, and washed in water. The total solids was 8%. They were tumbled with fine grained salt and sugar in aliquots, the salt and sugar added being such that at moisture contents of 55%, 45%, 35%, 30% and 20%, the final product would contain 10% of added salt and 10% of added sugar.

The parsley was dehydrated to approximately the predetermined moisture content. The finished product has the following composition:

<u>Sample</u>	<u>Water Activity</u>	<u>Moisture %</u>	<u>Freeze or Not</u> <u>at -20°C</u>
1	0.90	54	No
2	0.87	46	No
3	0.79	35	No
4	0.75	32	No
5	0.62	19	Yes - frozen

Samples 1 to 4 were flexible, in whole leaf form, had excellent colour and rehydrated to a product with fresh parsley aroma instantly when immersed in hot water.

EXAMPLE 3

Fresh Savoy cabbage was shredded, blanched in boiling water for 3 minutes and drained. The total solids content of the drained cabbage was 6%.

Four aliquots of 500g each of the drained blanched cabbage were tumbled for three minutes with fine grained salt and sugar so that an intimate mixture was obtained. The quantity of salt and sugar added to each aliquot was such that at final moisture contents of 60%, 45%, 35%, 25% and 15%, the

added salt content would be 5% and added sugar 5%.

The cabbage shreds were dehydrated to weights calculated to give the required moisture contents. The finished products had the following compositions:

<u>Sample</u>	<u>Water Activity</u>	<u>Moisture %</u>	<u>Freeze or Not at -20°C</u>
1	0.92	63	Yes
2	0.84	42	No
3	0.80	33.5	No
4	0.73	25	Partially
5	0.43	12	Yes

Samples 2 and 3 had a soft texture at -20°C, and rehydrated in 5 minutes when covered with boiling water to give a product with excellent natural colour, flavour and texture.

EXAMPLE 4

Fresh carrots were hand peeled and shredded into shreds 3mm x 3mm. The shreds were steam blanched for 3 minutes, at which stage they had a total solids content of 8%. Sufficient glycerol was mixed thoroughly with the blanched shreds such that at a moisture content of 30% finished product would contain 10% of glycerol. The shreds were then dried at 70°C to the predetermined moisture content 30%. The dried shreds containing 10% of glycerol remained quite flexible at -20°C.

The water activity was 0.71. On boiling in 20 parts by weight of water, they were tender and well rehydrated in three minutes, and had good colour and texture.

EXAMPLE 5

Some additional vegetables were preserved in accordance with the invention, and the results are shown as Figures 1 to 9

in the drawings, and in the tables provided below.

The vegetables were treated with salt (NaCl) solution so that they contained 5% added NaCl at the moisture levels specified. The vegetables were at a temperature of -20°C .

In the drawings, the symbol "o" indicates the treatment freezing was successful and the vegetables remained flexible and unfrozen at -20° in accordance with the invention, while the symbol "x" indicates an unsuccessful result, whereby the vegetables froze solid.

Figure 1 shows the results of preserving sliced potatoes in accordance with the invention as specified in the following table:

<u>Sample</u>	<u>Water Activity (Aw)</u>	<u>Moisture %</u>	<u>Frozen Solid?</u>
1	0.92	43	Yes
2	0.87	36	No
3	0.80	25	No
4	0.78	22	No
5	0.73	18	No
6	0.68	15	Yes
7	0.64	14	Yes

Figure 2 shows the results of preserving spinach as specified in the following table:

<u>Sample</u>	<u>Aw</u>	<u>Moisture %</u>	<u>Frozen Solid?</u>
1	0.90	55	Yes
2	0.89	52	Yes
3	0.83	40	No
4	0.82	32	No
5	0.80	30	No
6	0.72	28	No
7	0.58	18	Yes

Figure 3 shows the results of preserving carrot shreds as specified in the following table:

<u>Sample</u>	<u>Aw</u>	<u>Moisture %</u>	<u>Frozen Solid?</u>
1	0.86	46	Yes
2	0.82	40	No
3	0.81	37	No
4	0.77	33	No
5	0.71	27	No
6	0.63	20	No
7	0.53	16	Yes

Figure 4 shows the results of preserving sliced zucchini as specified in the following table:

<u>Sample</u>	<u>Aw</u>	<u>Moisture %</u>	<u>Frozen Solid?</u>
1	0.87	49	Yes
2	0.83	42	No
3	0.82	41	No
4	0.76	34	No
5	0.73	30	No
6	0.64	27	No
7	0.51	19	Yes

Figure 5 shows the results of preserving green peas as specified in the table below:

<u>Sample</u>	<u>Aw</u>	<u>Moisture %</u>	<u>Frozen Solid?</u>
1	0.91	53	Yes
2	0.88	36	No
3	0.79	27	No
4	0.78	24	No
5	0.72	21	No
6	0.67	17	Yes
7	0.62	14	Yes

Figure 6 shows the results of preserving diced tomatoes as specified in the table below:

<u>Sample</u>	<u>Aw</u>	<u>Moisture %</u>	<u>Frozen Solid?</u>
1	0.71	31	No
2	0.65	28	No
3	0.56	26	No
4	0.52	23	No
5	0.49	20	Yes

Figure 7 shows the results of preserving green onion tops as specified in the table below:

<u>Sample</u>	<u>Aw</u>	<u>Moisture %</u>	<u>Frozen Solid?</u>
1	0.88	59	Yes
2	0.84	51	No
3	0.83	46	No
4	0.66	28	No
5	0.49	14	Yes

Figure 8 shows the results of preserving green bell peppers as specified in the table below:

<u>Sample</u>	<u>Aw</u>	<u>Moisture %</u>	<u>Frozen Solid?</u>
1	0.87	60	Yes
2	0.82	49	No
3	0.70	34	No
4	0.56	20	Yes
5	0.40	13	Yes

Figure 9 shows the results of preserving sliced onions as specified in the table below:

<u>Sample</u>	<u>Aw</u>	<u>Moisture %</u>	<u>Frozen Solid?</u>
1	0.94	67	Yes
2	0.91	53	Yes
3	0.88	43	No
4	0.83	25	No
5	0.61	15	Yes

The above description is only illustrative of the invention, and obvious alterations and modifications may be made without departing from the spirit of the invention.

The claims defining the invention are as follows:

1. A method for preserving a vegetable product at sub-zero temperatures which comprises firstly treating said product by partially dehydrating and adding to said product at least one water activity controlling substance whereby the water activity is less than 1 (measured at 20°C), the moisture content is less than that of the untreated vegetable product, and both said water activity and moisture content is within a range whereby said product remains flexible and unfrozen at typical sub-zero frozen food storage temperatures, and secondly reducing the temperature of said product to a typical sub-zero frozen food storage temperture.
2. The method of claim 1, whereby said water activity controlling substance is added at the same time as, or before, partially dehydrating said product.
3. The method of claim 1, whereby said product is partially dehydrated before adding said water activity controlling substance.
4. The method of claim 1 wherein said water activity is within a range of from 0.5 to 0.9 (measured at 20°C) and said moisture content is within a range of from 20 to 50%.
5. The method of claim 1 wherein said water activity is within a range of from 0.7 to 0.85 (measured at 20°C) and said moisture content is within a range of from 25 to 45%.
6. The method of claim 1 wherein said water activity controlling substance is selected from one or more of sodium chloride, sodium citrate, potassium chloride, sucrose, dextrose, invert sugars, glycerol, sorbitol and propylene

glycol.

7. The method of claim 1 wherein the typical frozen food storage temperature is about -20°C .

8. Vegetable product preserved at a typical sub-zero frozen food storage temperature which has been partially dehydrated and to which at least one water activity controlling substance has previously been added, characterized in that said product has a water activity less than 1 (measured at 20°), a moisture content less than that of the unpreserved vegetable product, and both said water activity and moisture content is within a range whereby said product remains flexible and unfrozen at typical sub-zero frozen food storage temperatures.

9. The vegetable product of claim 8 wherein said water activity is within a range of from 0.5 to 0.9 (measured at 20°) and said moisture content is within a range of from 20 to 50%.

10. The vegetable product of claim 8 wherein said water activity is within a range of from 0.7 to 0.85 (measured at 20°) and said moisture content is within a range of from 25 to 45%.

11. The vegetable product of claim 8 wherein said water activity controlling substance is selected from one or more of sodium chloride, sodium citrate, potassium chloride, sucrose, dextrose, invert sugars, glycerol, sorbitol and propylene glycol.

12. The vegetable product of claim 8 wherein the typical frozen food storage temperature is about -20°C .

13. A vegetable product substantially as herein described with reference to any one of the Examples.

DATED this 11th day of October, 1989.

BYRON AGRICULTURAL COMPANY
PTY. LTD.
By Its Patent Attorneys
ARTHUR S. CAVE & CO.